#### TITLE

# METHOD FOR PREVENTING FORMATION OF PHOTORESIST SCUM

#### BACKGROUND OF THE INVENTION

### Field of the Invention

The invention relates to a semiconductor process, and more particularly to a method for preventing formation of photoresist scum in order to improve etching profile and prevent clogging of via holes, thus improving subsequent metallization.

### 10 Description of the Related Art:

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In current semiconductor integrated circuit method, the photolithography technique is a very critical procedure, in which accurate transfer of the circuit design to the semiconductor substrate determines the product properties. Generally, photolithography technique includes coating, exposure, development, and photoresist stripping. In recent years, with continuous miniaturization in device size, photolithography techniques require improvement and play an even more critical role in device quality, yield, and cost.

In the dual damascene photolithography method, nitrogen (N) reacts with and contaminates the photoresist. Thus, during the development procedure, amine (NH<sub>x</sub>) photoresist scum remains, in turn forming an inaccurate pattern and seriously affecting the electrical properties of the device.

The nitrogen source is derived from silicon oxynitride (SiON) material of the anti-reflective layer (ARL) and the silicon nitride or silicon carbon nitride (SiCN) material of

the etching stop layer. In order to further understand the background of the present invention, the conventional method for forming a dual damascene structure is explained accompanied by FIGS. 1a to 1e.

First, in FIG. 1a, an etching stop layer 102 such as silicon nitride or silicon carbon nitride, a dielectric layer 104, an anti-reflective layer 106 such as silicon oxynitride, and a photoresist layer 108 are formed in sequence on a substrate 100.

Subsequently, in FIG. 1b, a photoresist pattern layer 108a is formed using exposure and wet development. Since the photoresist layer 108 is contaminated by nitrogen, the photochemical reaction is not complete during exposure. Thus, during wet development, photoresist scum 108b remains on the sidewalls of the photoresist pattern layer 108a. Therefore, when etching is performed to form a via hole 104a, the etching profile is inferior and the critical dimension (CD) is changed as shown in FIG. 1c, seriously effecting the electrical properties of the device.

Subsequently, in FIG. 1d, after the photoresist pattern layer 108a is removed, a photoresist layer 110 is formed on the anti-reflective layer 106 and in the via hole.

Finally, in FIG. 1e, a photoresist pattern layer 110a is formed on the anti-reflective layer 106 by exposure and development. Next, etching is performed to form a trench 104b over the via hole 104a, making up a dual damascene structure. In the same way, due to nitrogen contamination during the exposure and development methods, photoresist scum 110b,

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detrimental to subsequent metallization and causing device failure, and is very difficult to remove even by photoresist stripping.

In order to solve the above-mentioned problem, plasma descumming with oxygen plasma is performed on photoresist pattern layers suffering formation of photoresist scum. However, after plasma descumming, the photoresist pattern layer thins and has decreased etching resistance. Also, the resulting pattern will be larger than the original design, which in turn changes the electrical properties of the device and does not meet the original device requirements.

In addition, some researchers have developed special photoresists or developers to prevent formation of photoresist scum. Although the photoresist scum problem is solved, the production cost increases.

#### SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a method for preventing formation of photoresist scum by means of using a non-nitrogen material as the anti-reflective layer to prevent nitrogen from contaminating the photoresist.

Another object of the present invention is to provide a method of preventing formation of photoresist scum by sandwiching the anti-reflective layer with two barrier layers and forming a barrier layer on the etching stop layer in order to prevent nitrogen from diffusing into the dielectric layer.

According to the object of the invention, a method for preventing formation of photoresist scum includes the

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following steps. A substrate on which a dielectric layer is formed is provided. Next, a non-nitrogen anti-reflective layer is formed on the dielectric layer. Finally, photoresist pattern layer is formed on the non-nitrogen anti-reflective layer. During the formation photoresist pattern layer, the non-nitrogen anti-reflective layer does not react with the photoresist pattern layer, thus not forming photoresist scum. The non-nitrogen antilayer can be silicon-rich oxide reflective  $(SiO_x)$ hydrocarbon-containing silicon-rich oxide  $(SiO_xC_v:$ H), where x < 2.

The present invention also provides а method preventing formation of photoresist scum suitable for a dual damascene process and the method of preventing formation of 15 photoresist scum includes the following steps. A substrate on which an etching stop layer, a dielectric layer, a first barrier layer, and an anti-reflective layer are formed is provided. The first barrier layer blocks a first dopant in the anti-reflective layer from diffusing into the dielectric Next, the anti-reflective layer, the first barrier layer, and the dielectric layer are etched to form a via Next, a photoresist pattern layer is formed on the anti-reflective layer and a protective plug is filled in the via hole. The first barrier layer blocks the first dopant 25 in order to prevent photoresist scum forming in the via hole. Finally, the anti-reflective layer, the first barrier and the dielectric layer are etched using the photoresist pattern layer and the protective plug as a mask to form a trench above the via hole, thus forming a dual 30 damascene structure. The method can further include forming

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a second barrier layer between the etching stop layer and the dielectric layer in order to block a second dopant in the etching stop layer from diffusing into the dielectric layer. Moreover, the method can further include forming a third barrier on the anti-reflective layer. The first, second, and third barrier layers can be silicon-rich oxide  $(SiO_x)$  or hydrocarbon-containing silicon oxide  $(SiO_xC_y:H)$ , where x<2, and have a thickness of 50 to 1000A. The first and second dopants can be nitrogen.

## 10 DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawings, given by way of illustration only and thus not intended to be limitative of the present invention.

15 FIGS. 1a to 1e are cross-sections illustrating the conventional method flow of forming a dual damascene structure.

FIGS. 2a to 2e are cross-sections illustrating the method flow of forming a dual damascene structure according to a first embodiment of the present invention.

FIGS. 3a to 3e are cross-sections illustrating the method flow of forming a dual damascene structure according to a second embodiment of the present invention.

FIG. 4 is a cross-section illustrating another initial step of the method flow of forming a dual damascene structure according to a second embodiment of the present invention.

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### DETAILED DESCRIPTION OF THE INVENTION

FIGS. 2a to 2e are cross-sections illustrating the method flow of preventing formation of photoresist scum according to a first embodiment of the present invention.

First, in FIG. 2a, a substrate 200 such as a silicon wafer is provided. Although there are semiconductor devices formed on the substrate 200, a flat substrate is depicted for simplicity. Next, an etching stop layer 202, a barrier layer 203, and a dielectric layer 204 are successively formed on the substrate 200. The material of the etching stop layer 202 can constitute silicon nitride or silicon carbon nitride. The barrier layer 203 can comprise siliconrich oxide  $(SiO_x)$  or hydrocarbon-containing silicon-rich oxide ( $SiO_xC_y$ :H), where x<2, having a thickness of 50 to 1000  $\mbox{\normalfont{A}}$  to block the dopant such as nitrogen in the etching stop layer 202 from diffusing into the dielectric layer 204. In addition, in the present embodiment, the etching stop layer 202 can also use material containing no nitrogen, such silicon-rich oxide (SiO<sub>x</sub>) or hydrocarbon-containing silicon-rich oxide  $(SiO_xC_y:H)$ , where x<2. In this way, there is no need to form the above-mentioned barrier layer Next, a non-nitrogen anti-reflective layer 206 and a photoresist layer 208 are formed on the dielectric layer 204. The non-nitrogen anti-reflective layer 206 can be silicon-rich oxide  $(SiO_x)$  or hydrocarbon-containing siliconrich oxide ( $SiO_xC_y$ :H), where x<2.

Subsequently, in FIG. 2b, a photoresist pattern layer 208a is formed using conventional exposure and wet development procedures. Since the non-nitrogen anti-

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reflective layer 206 contains no nitrogen, the photoresist 208 does not react with nitrogen during the photolithography method. That is, during wet development, photoresist scum remains on the sidewalls of photoresist pattern layer 208a.

Subsequently, in FIG. 2c, the non-nitrogen antireflective layer 206, the dielectric layer 204, and the layer 203 are etched in sequence using photoresist pattern layer 208a as an etching mask, thus exposing the etching stop layer 202 surface and forming a via hole 204a. Since there is no photoresist scum, the via hole 204a has a better profile. In addition, since no plasma descumming is required, the critical dimension (CD) does not change.

Next, in FIG. 2d, the photoresist pattern layer 208a is removed to expose the surface of the non-nitrogen anti-reflective layer 206. Next, a protective plug 209 is filled in the via hole 204a, such as i-line photoresist, to prevent the etching stop layer 202 from overetching, exposing the substrate 200. Next, a photoresist layer 210 is formed on the non-nitrogen anti-reflective layer 206 and on the protective plug 209 in the via hole 204a.

Finally, in FIG. 2e, a photoresist pattern layer 210a is formed using the exposure and development procedures. In the same way, the photoresist pattern layer 210a does not react with the non-nitrogen anti-reflective layer 206 to form residual scum. On the other side, although the etching stop layer 202 contains nitrogen, nitrogen cannot diffuse into the dielectric layer 204 because it is blocked by the barrier layer 203. Thus, the photoresist layer 210 in the

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via hole 204a will not be contaminated, and no photoresist scum forms in the via hole 204a. Next, the non-nitrogen anti-reflective layer 206 and the dielectric layer 204 are successively etched using the photoresist pattern layer 210a and the protective plug 209 as a mask to form a trench 204b above the via hole 204a, making up a dual damascene structure.

FIGS. 3a to 3e are cross-sections illustrating the method flow of preventing formation of photoresist scum according to a second embodiment of the present invention.

First, in FIG. 3a, a substrate 300, such as a silicon Next, an etching stop layer 302, a wafer is provided. barrier layer 303, a dielectric layer 304, a barrier layer 305, an anti-reflective layer 306, and a photoresist layer 308 are formed on the substrate 300 in sequence. The etching stop layer 302 can comprise silicon nitride or silicon carbon nitride. The anti-reflective layer 306 can be silicon oxynitride. The barrier layers 305 and 303 can comprise silicon-rich oxide  $(SiO_x)$  or hydrocarbon-containing silicon-rich oxide ( $SiO_xC_y$ :H), where x<2, having a thickness of 50 to 1000 Å to block the dopant, such as nitrogen, in the etching stop layer 302 and in the anti-reflective layer 306 from diffusing into the dielectric layer 304.

Subsequently, in FIG. 3b, a photoresist pattern layer 308a is formed using conventional exposure and wet development procedures. Next, in FIG. 3c, the anti-reflective layer 306, the barrier layer 305, the dielectric layer 304, and the barrier layer 303 are etched in sequence using the photoresist pattern layer 308a as an etching mask,

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thus exposing the surface of the etching stop layer 302 and forming the via hole 304a.

Subsequently, in FIG. 3d, the photoresist pattern layer 308a is removed to expose the surface of the anti-reflective layer 306. Next, a protective plug 309 is filled in the via hole 304a, such as i-line photoresist, to prevent the etching stop layer 302 from overetching, exposing the substrate 300. Next, a photoresist layer 310 is formed on the anti-reflective layer 306 and on the protective plug 309 in the via hole 304a.

Finally, in FIG. 3e, a photoresist pattern layer 310a is formed using the exposure and development procedures. the same way, during the photolithography method, although the anti-reflective layer 306 and the etching stop layer 302 contain nitrogen, nitrogen cannot diffuse into the dielectric layer 304 because of the blocking of the barrier layers 305 and 303 respectively. Thus, the photoresist layer 310 in the via hole 304a will not be contaminated, and there is no photoresist scum clogging of the via hole 304a, thus improving the subsequent metallization. Next, the nonnitrogen anti-reflective layer 306 and the dielectric layer 304 are successively etched using the photoresist pattern layer 310a and the protective plug 309 as a mask to form a trench 304b above the via hole 304a, making up a dual damascene structure.

In addition, in FIG. 3a, it is noted that a barrier layer 307 can be optionally formed between the anti-reflective layer 306 and the photoresist layer 308, as shown in FIG. 4. The barrier layer 307 can comprise silicon-rich oxide  $(SiO_x)$  or hydrocarbon-containing silicon-rich oxide

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(SiO $_x$ C $_y$ :H), where x<2, having a thickness of 50 to 1000 Å to further block the dopant, such as nitrogen, in the antireflective layer 306 from diffusing into the dielectric layer 304.

According to the inventive method, photoresist scum is effectively prevented by the use of the non-nitrogen material as the anti-reflective layer, the etching stop layer, or the barrier layer. In addition, since no plasma descumming is required and no special photoresist or developer is used, the critical dimension does not change and the production cost is decreased.

While the invention has been described by way of example and in terms of the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. To the contrary, it is intended to cover various modifications and similar arrangements (as would be apparent to those skilled in the art). Therefore, the scope of the appended claims should be accorded the broadest interpretation so as to encompass all such modifications and similar arrangements.